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Production of solketal (2,2-Dimethyl-1,3-dioxolane-4-methanol) from glycerol and acetone by using homogenous acidic catalyst at the boiling temperature (preliminary study)

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Abstract. Currently, solketal is produced from glycerol and acetone by using heterogeneous catalyst. However, a solid heterogeneous catalyst is not preferable since water contained in the glycerol, is adsorbed on the surface of the catalyst. Water could act as inhibitor in the reaction and lowering the activity of the catalyst. Therefore, homogenous acid catalyst is proposed to avoid the inhibition during the reaction. The aim of this research was to utilize sulphuric acid as the homogenous acid catalyst, to explore the effect of the mole ratio glycerol:acetone to the conversion, and determine the entropy and enthalpy of the reaction. The process was carried out in a three neck reactor equipped with a heater, temperature control, cooler and stirrer. The reaction conditions were set at a constant boiling temperature, the reaction time was varied at 4 - 12 h, and the mole ratio of acetone to glycerol was varied in the range of 2:1 - 7:1. Results indicated that the highest conversion (>80 %) was recorded at 62°C, 10 h, and 6.9:1 mole ratio. The conversion of glycerol to solketal was influenced by mole ratio which is consistent to Le Chatelier principle. From the entropy ($\Delta S = 280.02 \text{ J. mole}^{-1} \text{ K}^{-1}$) and enthalpy ($\Delta H = 95.948 \text{ J. mole}^{-1}$), it can be concluded that the reaction of solketal formation was exothermic.

Keywords: acetone; catalyst; glycerol; solketal; sulphuric acid;

1. Introduction

Currently, the production of renewable energy is increasing worldwide. Fossil fuels, which are non-renewable fuels, and the problem of environmental pollutions have driven the demand of the renewable energy [1], [2] [3]. Indonesia is well known as the largest palm oil producer in the world. Recently, biodiesel produced from the palm oil is growing rapidly. Biodiesel is an ester of triglycerides and alkyl is produced by transesterification reaction. Biodiesel is an alkyl ester often named FAME (Fatty acid methyl ester) is produced by the transesterification of oil or fat with alcohol



in an alkaline atmosphere. However, during the mass scale production, the presence of glycerol as a byproduct is also generated. This condition have impacted on the price of glycerol that drops drastically due to overproduction. Utilization of glycerol to high value products seems promising to avoid this problem. One of the promising derivative products from glycerol is solketal which is potential as an additive fuel [1],[2],[3].

Solketal is commonly produced by reacting glycerol and acetone using heterogeneous catalyst with or without the presence of solvents [4] [5]. However, the presence of water in glycerol needs to be avoided. Latest researcher reported that water could generate reverse reaction and lowering the activity of heterogeneous catalysts in the reaction [5] [6]. Another problem is the conversion of glycerol to solketal which is still low. To obtain high conversions of glycerol, excess amount of acetone could be supplied or by removing the water generated during the reaction continuously [7]. Previous research employed microwave assisted and solvent free reaction to avoid the presence of water [5]. However, the method is not suitable to be used at the large scale production. Based on this case, the utilization of homogenous acid catalyst such as sulphuric acid seems promising since water could not compete with the catalyst. However, based on our knowledge, the utilization of the sulphuric acid as the catalyst to produce solketal is still not explored so far.

The objective of this study was to determine the thermodynamic parameters such as entropy and enthalpy of the production of solketal from acetone and glycerol by using homogeneous acid catalyst at the boiling temperature without solvent. In the preliminary study, the condition of equilibrium was studied. Subsequent studies of the reaction were then carried out at a variation of the mole ratio (acetone / glycerol) in various ranges (2: 1 - 7: 1) mol/mol at a mixed boiling temperature for 9-12 h or until the conversion is constant. In this study, the reaction was carried out at the boiling temperature without solvent, in order to reduce reaction time and cost.

2. Material and methods

2.1 Material

Glycerol (85% w/w purity) and acetone (96 % w/w purity) were purchased from Sigma-Aldrich. Sulphuric acid (98% w/w purity) was used as the catalyst. Sulfuric acid was selected as the catalyst due to high tolerance of water.

2.2. Synthesis of Solketal from Glycerol and Acetone

Acetone and glycerol at different mole ratios were mixed in a three-neck flask equipped with temperature controllers, stirrers, thermometers and condensers. The weight ratio of the catalyst to reactant was 2% w/w. At the same time, the cooling water was recirculated to condense the vapor to return to the three-neck flask. Initial reaction time (0 h) was determined when the reactant reached boiling temperature of the mixture. The reaction was run at a constant temperature for 4 -12 h. At the end of reaction, excess acetone was separated from the mixture by using distillation at 56°C. Excess acetone collected from distillation was measured to determine the density, purity and mole of acetone. Glycerol conversion was calculated indirectly by using mole of excess acetone. Analysis of the product was performed at any reaction time. Fourier Transform Infra Red (FTIR) analysis was performed to prove the chemical structure of the solketal.

2.3. Analysis

2.3.1. Analysis of chemical structure of Solketal using FTIR. In this study, FTIR spectrophotometer (Paragon 1000PC Perkin Elmer) was used to analyze the functional groups of solketal molecules that had been produced by the reaction. Analysis was performed to identify the presence of functional groups which was characterized in the form of spectra.

2.3.2. Determination of glycerol conversion. Equation 1 and 2 were used to determine the conversion of the reaction. The mole acetone reacted was determined by calculating the mole of acetone before and after the reaction. Glycerol conversion was calculated based on the number of acetone moles used to react with glycerol.

$$x = \frac{[G]_0 - [G]_t}{[G]_0} \quad (\text{Eq. 1})$$

$$[G]_0 - [G]_t = [A]_0 - [A]_t \quad (\text{Eq. 2})$$

where x is conversion of glycerol, $[G]_0$ is the initial mole of glycerol, $[G]_t$ is the mole of glycerol at certain time, $[A]_0$ is the initial mole of acetone, and $[A]_t$ is the mole of acetone at certain time.

2.3.3. Determination of thermodynamic parameters The equilibrium reaction is a two-way reaction in which each product formation is always followed by the decomposition of the product back into a reactant. When the rate of product formation is equal to the rate decomposition of a product, the equilibrium condition is achieved. A desirable high reactant conversion is achieved when the reaction of product formation is faster than the product decomposition reaction. There are several methods for shifting the reaction to the formation of the product: among others are one of the reactants is made in excess concentration so that the reaction shifts toward the formation of the product. In this study, one of the reactants ie acetone is made excess. In this study, the mole ratio of acetone: glycerol was varied in the range of 2: 1 to 7: 1.

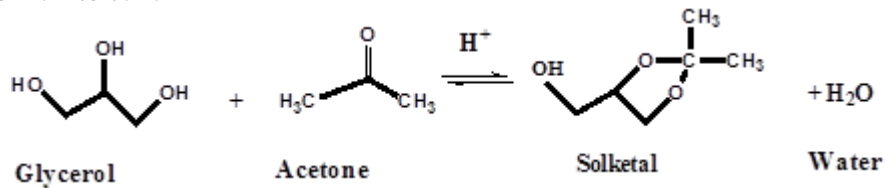
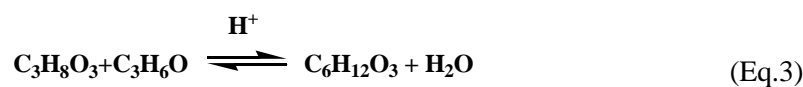


Fig. 3. The reaction of Solketal production from Acetone and Glycerol [4]

In a more concise form the solketal formation reaction were written in the form of a molecular structure as in Eq.3 and 4



Where A is glycerol, B is acetone, C is solketal and D is water. Limiting reactan is set to A. The reaction rate was expressed in Eq.5.

$$-r_A = k_1 C_A^a C_B^b \rightleftharpoons k_2 C_C^c C_D^d \quad (\text{Eq. 5})$$

$$M = \frac{N_{B0}}{N_{A0}} \quad (\text{Eq.6})$$

For a liquid phase reaction, the thermodynamic equilibrium can be expressed as an equilibrium concentration (K_C) using Eq. 7, Eq. 8, and Eq. 9.

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (\text{Eq.7})$$

$$\Delta G^0 = -RT \ln K_C \quad (\text{Eq.8})$$

Where K_C

$$K_C = \frac{k_1}{k_2} = \frac{[C_C]^c [C_D]^d}{[C_A]^a [C_B]^b} \quad (\text{Eq.9})$$

Entropy and enthalpy was determined from the equation (Eq. 10)

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R T} \quad (\text{Eq.10})$$

Where ΔS^0 is the standard entropy at 298 K in the unit of $(\text{kJ mol}^{-1}\text{K}^{-1})$, ΔH^0 is the standard enthalpy at 298 K (kJ mol^{-1}) , R is the universal gas constant $(\text{kJ mol}^{-1}\text{K}^{-1})$ and T is reaction temperature (K).

Equilibrium constant K_C is a function of product concentration and reactant concentration at equilibrium condition (Eq.9). Therefore, concentrations equal to moles ($C_{i,eq}$) was determined if the conversion at equilibrium conditions was known as shown in Eq.11

$$C_{i,eq} = \frac{N_{i,eq} \times 1000}{V_m} (\text{mole l}^{-1}) \quad (\text{Eq. 11})$$

where $N_{i,eq}$ = mole of i component at equilibrium condition, V_m is the volume of solution in the reactor (ml).

In this study the glycerol mole at equilibrium ($N_{A,eq}$) was expressed by Eq. 12

$$N_{A,eq} = N_{A0} - N_{A0} x_{eq} \quad (\text{Eq. 12})$$

Where N_{A0} is mole of glycerol at the time of reaction ($t = 0$), x_{eq} is the conversion of glycerol at the equilibrium condition. Mole of other components at equilibrium conditions can be calculated on the basis of the equation. When the reaction is in an equilibrium state, the component concentration is expressed as a mole of acetone = $C_{B,eq}$, mole of glycerol = $C_{A,eq}$, mole of Solketal = $C_{C,eq}$ and mole of water = $C_{D,eq}$. where the concentration of each component was determined using the equation (Eq.13- Eq. 16),

$$N_{B,eq} = N_{B0} - N_{A0} x_{eq} = N_{A0} (M - x_{eq}) \quad (\text{Eq.13})$$

$$N_{C,eq} = N_{C0} + N_{A0} x_{eq} \quad (\text{Eq. 14})$$

$$N_{D,eq} = N_{D0} + N_{A0} x_{eq} \quad (\text{Eq.15})$$

$$K_C = \frac{C_{C,eq}^c C_{D,eq}^d}{C_{A,eq}^a C_{B,eq}^b} \quad (\text{Eq.16})$$

In this study K (the equilibrium constant) was calculated by the conversion of glycerol which was analyzed at the varied reaction time. Glycerol conversion was shown in the Table 3. The concentration of components in the mixture was analyzed indirectly by separating unreacted acetone. Reacted acetone to glycerol was determined by calculating the difference of moles before and after the reaction. In accordance with the stoichiometry, the amount of reacted acetone mole is equal to glycerol. In this research, the initial glycerol concentration was set to C_{A0} = mole/ liter.

3. Result and Discussion

3.1. Analysis of solketal formation

The chemical structure of the solketal was shown in Figure 1 [8]. The result of FTIR showed the absorption of compounds at different wavelengths (Figure 2). The chemical chain structure of the solketal compound was listed in Table 1. Results showed that the chemical structure of the solketal was composed from carbon compound with two ethers (-O-) group attached to one carbon atom (C) tertiary.

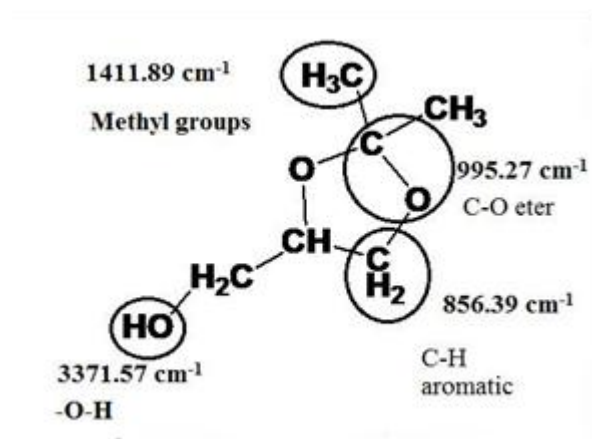


Figure 1. The chemical structure of solketal and the wave number that indicating the specific functional group of the molecule [4]

Figure 2 proved that the solketal formed was marked by the FTIR peak at the wave number of 995.27 cm⁻¹. It was also indicated by the NIST in Table 1. The product solketal was also shown by the peak of FTIR at 856.39 cm⁻¹ indicating the presence of an aromatic C-H function group possessed in the structure of solketal. The absorbance peak of the OH (hydroxyl) group appeared on the wave number of 3.371 cm⁻¹ and the methyl group at the wave number 1.411 cm⁻¹. From the analysis it can be concluded that solketal was formed by reacting the acetone and glycerol by using sulphuric acid as the catalyst.

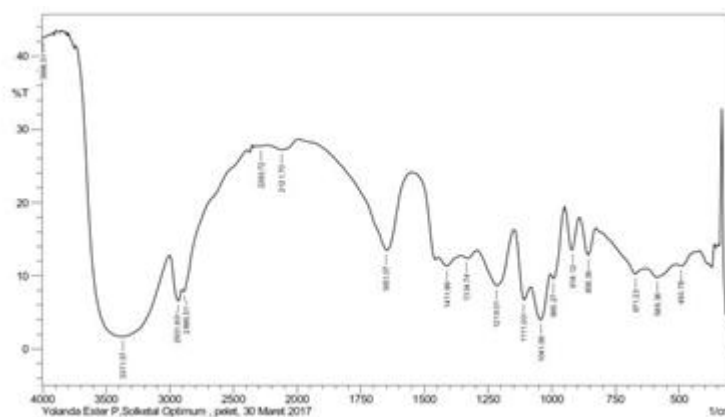


Figure 2. Analysis of the solketal molecular structure using FTIR

Tabel 1. Result of FTIR analysis of Solketal

Wave number (cm ⁻¹)	Wave Number of Fungtional group of Solketal From Refference (NIST)	Fungtional Groups
671.23	-	C-H aromatic
856.39	875	C-H aromatic
918.12	900	C-H aromatic
995.27	995	C-O eter conjugation
1041.56	1100	C-O eter conjugation
1111.0	1200	C-O eter conjugation
1219.01	1250	C-O eter conjugation
1334.74	-	-
1411.89	1375	Methyl groups
-	1475	C-H aromatik
-	1740	C=O aldehida
1651.07	-	C=O (Amida) and C=C (Alkane)
2283.72	-	-
2885.51	2800-2900	C-H aldehida weak
2931.8	2999	Alkil groups
3371.57	-	embded O-H
	3650-3600	Free O-H

3.2. Determination of thermodynamic parameters

The reaction in solketal synthesis using acetone and glycerol feedstock is equilibrium reaction. Chemical equilibrium is a state where there is no chemical reaction occurring between the various objects, or any transfer of matter from one part of the system to another part due to any kind of diffusion. Thus, during chemical equilibrium, the chemical potential of the various systems remains constant. The chemical equilibrium changes if there are changes in the reaction conditions such as pressure, temperature and concentration of components present in the reaction system. Equilibrium condition does not necessarily mean that reactants and products are present in equal amounts. It means that the reaction has reached a point where the concentrations of the reactant and product are unchanging with time because the forward and backward reactions have the same as can be seen in Figure 3. The thermodynamic parameter relating to chemical equilibrium is Gibbs free energy. Gibbs energy must be negative to drive the reaction. Gibbs energy in positive value means the reaction is very slow and the chemical process becomes uneconomical. Factors affecting Gibbs free energy are pressure, temperature and activity or concentration. The availability of chemical reaction can be seen from the equilibrium constants value. The equilibrium or K_C constants value depends on the free energy of Gibbs and changed through changing reaction conditions such that one of the reactants is made excessively beyond the stoichiometric requirement.

In this research, the effect of the mole ratios to the equilibrium constants was shown in Table 3 and Table 4. The equilibrium constants were proportional to the mole ratios. This results were also in accordance to Lechatelier principle which the reaction rate is proportional to the concentration of the reactants. The greater the concentration of the reactant supplied, the greater the rate of the reaction and the greater the equilibrium constants obtained.

Table 2 and Table 3 showed the conversion of glycerol under equilibrium conditions. Based on the result, the conversion was proportional to the mole ratio (Table 3). This is also in accordance with Lechatelier principle that the reaction is shifted to a smaller concentration until constant equilibrium is reached. Table 2 showed that the conversion was affected by the mole ratio of acetone and glycerol

which were proportional. The concentration increased when the value mole ratio was greater. The effect of the mole ratios to the equilibrium constants can be found in table 4.

Tabel 2. The result of reaction analysis at mixed boiling temperature at fixed reaction time 12 hours , Variation of Acetone / Glycerol mole ratios and reactant concentration at initial time. V_{A0} = Volume of Glycerol, V_{B0} = Volume of Acetone, ρ_A = Density of Glycerol, F_A = Purities of Glycerol, ρ_B = Density of Acetone, F_B = Purities of Acetone, W_A = Weight of Glycerol, W_B = Weight of Acetone, N_{A0} = Mole of Glycerol at initial, N_{B0} = Mole of Acetone at initial, V_T = Total volume, C_{A0} = Concentration of Glycerol at initial, C_{B0} = Concentration of Acetone at initial.

V_{A0} (ml)	ρ_A , (gr/ml)	F_A	V_{B0} (ml)	ρ_B (gr/ml)	F_B	W_A (gr)	W_B (gr)	N_{A0}	N_{B0}	V_T	C_{A0} , (mole/l)	C_{B0} (mole/l)
73.5	1.26	0.85	156	0.78	0.96	78.72	117.41	0.85	2.02	229.5	3.72	9.82
47.5	1.26	0.85	156	0.78	0.96	50.87	117.41	0.55	2.02	203.5	2.71	11.08
37.5	1.26	0.85	156	0.78	0.96	40.16	117.41	0.44	2.02	193.5	2.25	11.65
30.5	1.26	0.85	156	0.78	0.96	32.67	117.41	0.35	2.02	186.5	1.9	12.09
25.5	1.26	0.85	156	0.78	0.96	27.31	117.41	0.3	2.02	181.5	1.63	12.42

Tabel 3. The result of reaction analysis at mixed boiling temperature at fixed reaction time 12 hours , Variation of Acetone / Glycerol mole ratios and reaktant concentration at equilibrium condition. V_B = Volume of Acetone at equilibrium, $N_{B,eq}$ = Mole of Acetone at equilibrium, N_{BR} = Mole of B react, N_{AR} = Mole of A react, $C_{A,eq}$ = Concentration of A at equilibrium, x = Conversion of Glycerol, $C_{B,eq}$ = Concentration of B at equilibrium, $N_{C,eq}$ = Mole of Solketal at equilibrium, $C_{C,eq}$ =Concentration of Solketal at equilibrium, $N_{D,eq}$ = Mole of Water at equilibrium, $C_{D,eq}$ = Concentration of Water at equilibrium, K_C = Equilibruiuk constant, T = Temperature (K).

M	V_B	ρ_B	F_B	$N_{B,eq}$	N_{BR}	N_{AR}	$N_{A',eq}$	$C_{A,eq}$	X	$C_{B,eq}$
2.36	120.5	0.77	0.97	1.55	0.48	0.48	0.38	1.65	0.56	6.74
3.66	129.6	0.77	0.97	1.65	0.37	0.37	0.18	0.9	0.67	8.12
4.64	133.5	0.77	0.97	1.7	0.32	0.32	0.12	0.6	0.73	8.8
5.7	136.3	0.77	0.97	1.74	0.28	0.28	0.07	0.38	0.80	9.32
6.82	139.5	0.77	0.97	1.78	0.24	0.24	0.05	0.29	0.82	9.8

Tabel 4. The result of reaction analysis at mixed boiling temperature at fixed reaction time 12 hours , Variation of Acetone / Glycerol mole ratios and solketal and water concentration at equilibriumcondition

$N_{C,eq}$	$C_{C,eq}$	$N_{D,eq}$	$C_{D,eq}$	K_C	$\ln K_C$	$(1/T) 10^3$
0.48	2.07	1.39	6.07	1.13	0.12	2.93
0.37	1.82	1.05	5.18	1.29	0.25	2.95
0.32	1.65	0.92	4.73	1.48	0.39	2.97
0.28	1.52	0.82	4.38	1.89	0.63	2.98
0.24	1.34	0.73	4.03	1.87	0.63	2.99

In this work, each mole ratio was recorded at different boiling temperatures. The larger mole ratio presented, the lower the boiling temperature obtained. When the mole is increased, the composition of acetone is higher than glycerol. This condition resulted lower boiling temperature, which was nearly equal to the boiling temperature of acetone, since the boiling temperature of acetone is lower than glycerol.

The effect of temperature on the conversion and the equilibrium constants can be found in Table 4 and Figure 4. Figure 4 showed that the conversion was proportional to the ratio mole (M). Table 4 also showed that the equilibrium constant is inversely proportional to the temperature. Equilibrium constant was higher when the temperature decreased. This indicated that the reaction was exothermic. This condition is also in accordance with the Lechatelier principle for exothermic reactions stating that the lower the temperature recorded, the faster the reaction occur, and equilibrium constants are increasing.

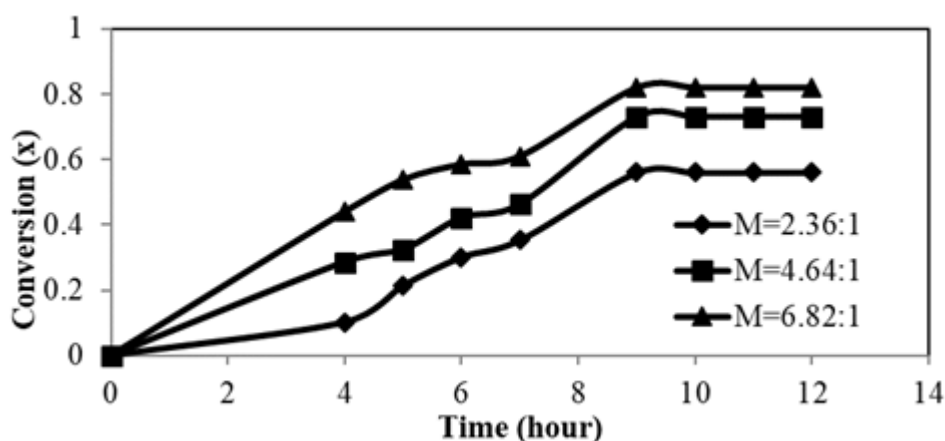


Figure 3 Graph of the relationship between reaction time to Glycerol conversion at different mole ratio of Acetone/Glycerol. The reaction is carried out at a mixed boiling temperature

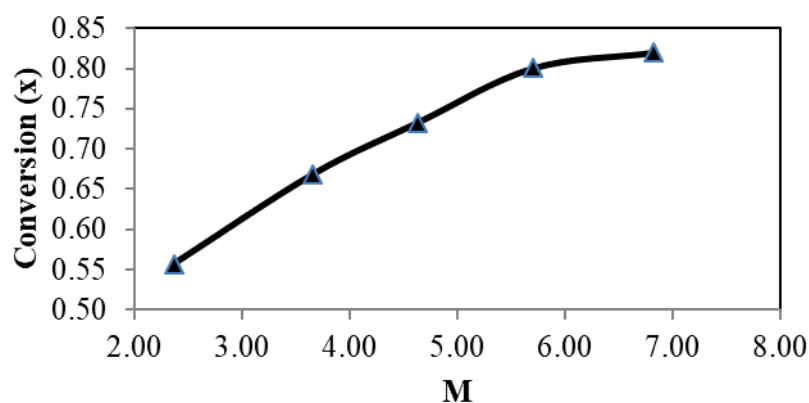


Figure 4. Effect of mole ratio of Acetone / Glycerol to glycerol conversion, at reaction time of ten until twelve hours at mixed boiling temperature.

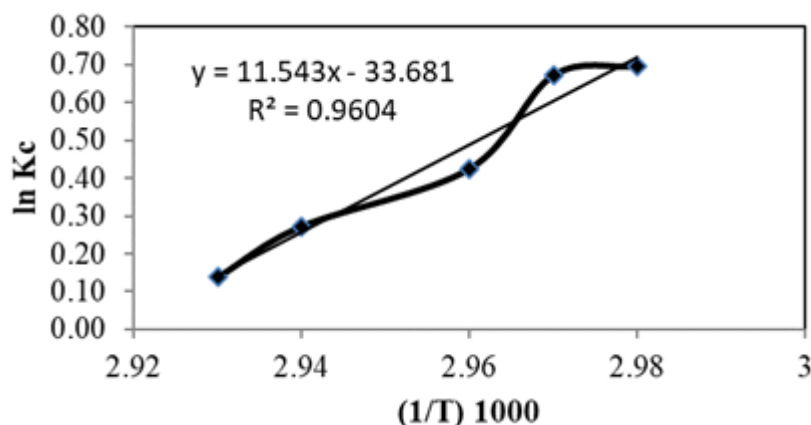


Figure 5 Graph of the relationship between $\ln K_c$ Vs $(1/T)$

Thermodynamic analysis

Thermodynamic properties (entropy and enthalpy) were predicted by plotting a graph from the experimental data $\ln K_c$ Vs $1/T$ (K^{-1}) as shown in Figure 5. It is recorded that $\Delta H/R$ is -11.54 and $\Delta S^0/R$ is -33.68. Where $\Delta H^0/R$ is the slope and $\Delta S^0/R$ is the intercept of trend line of Fig 5. Since the enthalpy of reaction ΔH is negative, the reaction is exothermic. This result is also in accordance with previous research [8].

4. Conclusion

This paper reported the preliminary study of solketal synthesized from glycerol and acetone using sulphuric acid as homogenous acid catalyst, at the varies boiling temperature of the mixture without using any solvents. The results of the FTIR analysis showed that the solketal can be synthesized using acetone and glycerol feedstocks in an acidic atmosphere. The reaction reached equilibrium at 10 hours. The highest conversion to glycerol was reached at 84%. The best condition was reached at the mole ratio 6.8:1, 62 °C, and 10 h reaction time. From the thermodynamic parameters, $\Delta H = 95.948 \text{ J (mole)}^{-1}$ and entropy $\Delta S = 280.02 \text{ J (mole K)}^{-1}$, it can be concluded that the reaction in this work was exothermic.

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